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METHANE POTENTIAL OF INDUSTRIAL OIL-CLAY BY-PRODUCT

Master Theses

Examiner: Professor Jukka Rintala
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ABSTRACT

TAMPERE UNIVERSITY OF TECHNOLOGY
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In this thesis suitability of industrial by-product oil-clay to produce biogas in anaerobic digestion was studied. Oil-clay (spent bleaching earth) contains high amounts of fats and clay (sand).

The methane production potential was studied by methane production batch assay with two mesophilic and one thermophilic inoculum. Methane production potential of oil-clay was high in all assays ranging from 532 to 664 l CH_4/kg substrate VS added and from 728 to 922 l CH_4/kg substrate VS removed. The yield was close to the theoretical maximum of fats. No inhibition caused by high lipid content of the substrate was observed, only some differences in the lag phase before the methane production initiated. Pretreatment with alkali increased the soluble COD but it did not have an effect on the methane production potential of oil-clay in batch assay. Thermal pretreatment had no effect on soluble COD levels. The behavior of oil-clay in the anaerobic digestion vessel was observed to be problematic, because of its tendency to float and after wetting sink quickly to the bottom. The spent oil-clay is acidic (pH 3.5) causing the need to adjust the pH before feeding it to the digester.

As a conclusion it can be postulated that oil-clay substrate used is a potent feedstock for methane production by anaerobic digestion. Its methane production potential is high and the volatile solids of the substrate are efficiently used for methanogenesis. However the acidic nature, high lipid content and behavior in the vessel need to be taken into account when planning full scale application. More studies with actual reactors and careful planning of the input amounts and processes are needed to evaluate this issue further.

TIIVISTELMÄ

TAMPEREEN TEKNILLINEN YLIOPISTO
Ympäristö- ja energiatekniikan koulutusohjelma
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Tässä diplomityössä tutkittiin teollisen öljy-savi-sivutuotteen sopivuutta biokaasun tuottamiseen anaerobisella prosessilla. Öljy-savi (puristekakku, joka sisältää suodatusjäänteet) sisältää runsaasti rasvoja sekä savesta peräisin olevaa hiekkaa.

Metaanituottopotentiaalia tutkittiin panoskokeilla käyttäen kahta mesofiilistä ja yhtä termofiilistä mikrobiymppiä. Öljy-saven metaanintuottopotentiaali oli korkea kaikilla ympeillä (532-664 l CH_4/syötetty VS, 728- 922 l CH_4/poistettu VS), lähellä teoreettista maksimia. Korkea lipidipitoisuus ei inhiboinut metaanin tuottoa. Pieniä eroja metaanin tuoton käynnistymisajankohdassa sen sijaan havaittiin. Alkalisella kemikaalilla tehty esikäsittely lisäsi liukoisen CODn määrää mutta sillä ei ollut vaikutusta metaanintuottopotentiaaliin panoskokeissa. Kuumentamalla tehty esikäsittely ei lisännyt liukoisen CODn määrää. Öljy-savi kellui ensin veden pinnalla ja upposi nopeasti vettymisen jälkeen. Öljy-savi on hapanta (pH 3.5), mistä johtuen pH tulee säätää ennen sen käsittelyä anaerobireaktorissa.

Tämän tutkimuksen johtopäätöksenä voidaan sanoa että tässä tutkittu öljy-savi soveltuu hyvin käytettäväksi metaanin tuottoon anaerobisessa käsittelyssä. Sen metaanintuottopotentiaali on korkea ja orgaaninen aines voidaan käyttää tehokkaasti metanogeneesissä. Sen happamuus, korkea rasvapitoisuus sekä käyttäytyminen reaktorissa on otettava huomioon, kun suunnitellaan käytännön sovelluksia. Tarvitaan lisätutkimuksia oikeilla reaktoreilla, jotta voidaan optimoida reaktorin kuormitus ja sekoitussuhde.

PREFACE

This study was carried out at the Department of Chemistry and Bioengineering, Tampere University of Technology under supervision of Professor Jukka Rintala. The master theses work was done in collaboration with Neste Oil Oyj. Neste Oil Oyj provided the funding and the material for the experimental part of this study.

I am grateful for Professor Rintala for his guidance, support and optimism during this short period of this study. I would like to express my warmest thanks to D.Sc. (tech.) Harri Heiskanen from Neste Jacobs for his valuable comments and interest to the study. Antti Nuottajärvi, Tarja Ylijoki-Kaiste and other staff of the department are acknowledged for their technical help during the experiments. And last but not least, I would like to express my thanks to Iiris Puhakka for her help and friendship during this process.

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Ylöjärvi, September 2014

Minna Valtavaara

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LIST OF SYMBOLS AND ABBREVIATIONS

BE	Bleaching earth
$Ca(OH)_2$	Calcium hydroxide
COD	Chemical oxygen demand
DM	Dry matter
KOH	Potassium hydroxide
LCFA	Long-chain fatty acid
N	Nitrogen
NaOH	Sodium hydroxide
OBE	Olive bleaching earth
OFMSW	Organic fraction of municipal solid waste
P	Phosphorus
rpm	Rounds per minute
RT	Room temperature
SBE	Spent bleaching earth
SRB	Sulfate reducing bacteria
SCOD	Soluble chemical oxygen demand
TS	Total solids
VFA	Volatile fatty acids
VS	Volatile solids
WAS	Waste-activated sludge

1 INTRODUCTION

Biogas, mostly consisting of methane and carbon dioxide, is produced in anaerobic digestion by micro-organisms specialized to it. Outputs of the process are biogas and digestate, which both can be used to further purposes with some limitations. Biogas is renewable energy with many positive effects when environment is concerned. Converting waste to biogas is an efficient way to decrease the amount of waste, to decrease the methane emission into the atmosphere and produce considerable amount of energy.

In this study the suitability of oil-clay (spent bleaching earth, SBE) that is a by-product of oil refinery industry to be used as substrate for anaerobic digestion was studied. Around 2 million tons of SBE is produced annually world-wide. SBE contains clay, high amount of lipids, color bodies etc. Several applications for SBE reuse or recycling, like regeneration, use for construction materials, use as fuel briquettes or for biodiesel production or for biogas production has been proposed. Because of its high fat content, it would be valuable material for biogas production instead of incineration of it. Not many studies of using SBE for production of biogas are published, but there are some biogas plants in Europe taking SBE as feedstock for production.

Because of the high lipid content of SBE, it is important to evaluate the initial methane production potential and the behavior of oil-clay in the reactor prior full scale reactor experiments. Clogging, flotation and washouts are caused by lipids in anaerobic digestion process. Lipids are hydrolyzed to glycerol and free long chain fatty acids (LCFA) in anaerobic process. LCFAs are known to cause inhibition of anaerobic digestion process by irreversible inhibition or by extending the lag phase (Angelidaki & Ahring 1992, Broughton et al. 1998, Cirne et al. 2007, Pereira et al. 2005, Salminen et al. 2000).

Pretreatment of the anaerobic digestion feedstock is used to enhance biomethane production. Several methods including thermal, chemical, milling, ultrasonication and biological pretreatment methods are available. The aim is to increase the biodegradation efficiency and improve biogas production by increasing the hydrolysis and availability of organic wastes. Different methods are used for different feedstock depending on its properties. In this study thermal and alkaline pretreatment methods were used.

The literature review of this work is focused on two main issues: firstly the anaerobic digestion process and factors involved in it and secondly to SBE, its uses and properties. To provide background information on SBE also clays in general are covered.

In the experimental part properties of oil-clay sample was studied. The methane production potential of the material was investigated with methane production batch assay. Also the effect of alkaline or thermal pretreatment and behavior of the material in the vessel were studied.

2 ANAEROBIC DIGESTION

Anaerobic digestion is mostly used for the treatment of waste sludge and high-strength organic wastes to produce biogas, containing methane and carbon dioxide. Anaerobic process (Figure 2.1.) is a series of individual steps carried out by different consortia of microorganisms each having different requirements on the environment (Angelidaki et al. 1993, Metcalf & Eddy 2003, Schink 1997, Weiland 2010).

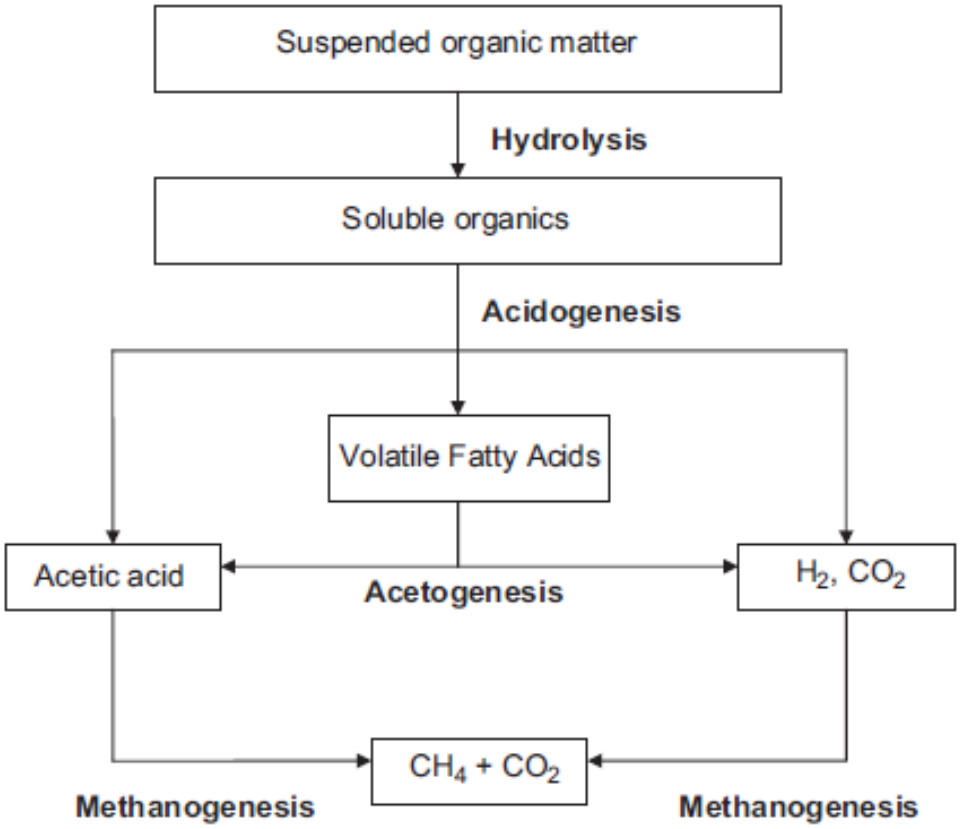


Figure 2.1 Anaerobic digestion process. (Appels et al. 2008)

The steps of anaerobic digestion are hydrolysis, acidogenesis, acetogenesis and methanogenesis. In hydrolyses step more complex polymers are hydrolyzed by bacteria into liquefied monomers and polymers. Lipids are hydrolyzed to fatty acids, polysaccharides to monosaccharides, proteins to amino acids and nucleic acids to purines and pyrimidines. Hydrolytic micro-organisms excrete hydrolytic enzymes like cellulose, cellobi-

ase, xylanase, amylase, lipase, protease etc. (Angelidaki et al. 1993, Metcalf & Eddy 2003, Schink 1997, Weiland 2010).

In acidogenesis (fermentation) amino acids, sugars and some fatty acids are degraded by acidogenic bacteria. Short chain volatile fatty acids (propionic acid, butyric acid, acetic acid, formic acid, lactic acid), ketones, alcohols, hydrogen and carbon dioxide are formed. Other products besides the hydrogen, carbon dioxide and acetic acid will go through acetogenesis. Most of the bacteria involved in hydrolysis and fermentation are strict anaerobes like *Bacteriocides*, *Clostridia* and *Bifidobacteria*. Also some facultative anaerobes like *Streptococci* and *Enterobacteriaceae* are involved in the processes. (Angelidaki et al. 1993, Metcalf & Eddy 2003, Schink 1997, Weiland 2010)

Acetogenesis transforms propionic acid, butyric acid and alcohols by acetogenic bacteria into hydrogen carbon dioxide and acetic acid. Acetogenic bacteria are inhibited by the accumulation of hydrogen. Therefore the hydrogen partial pressure has to be low enough to allow the conversion of all the acids. The pressure is lowered by hydrogen scavenging bacteria. Typical acetogenic bacteria include *Acetobacterium* and *Clostridium aceticum*. (Angelidaki et al. 1993, Metcalf & Eddy 2003, Schink 1997, Weiland 2010)

Methanogenic archea carry out methanogenesis by producing methane from acetate or hydrogen and carbon dioxide. There are two groups of methanogenic organisms, aceticlastic methanogens and hydrogen-utilizing methanogens. Aceticlastic methanogens split acetate into methane and CO_2 while hydrogen-utilizing methanogens use hydrogen and CO_2, to produce methane. Species that produce methane from acetate are limited, including e.g. *Methanosarcina barkeri*, *Metanonococcus mazei* and *Methenotrix soehngenii*. All methanogenic archea are capable of producing methane from hydrogen. (Angelidaki et al. 1993, Metcalf & Eddy 2003, Schink 1997, Weiland 2010)

2.1 Substrates for anaerobic digestion

Different feedstock for anaerobic digestion can be used, and their methane potentials vary. Theoretical methane production capacity for fats is around 1000 l CH_4 / kg volatile solids (VS), when for proteins it is 480 l CH_4 / kg VS and for carbohydrates 400 l CH_4 / kg VS (Wellinger et al. 2013). Animal manure, rendering house waste, sewage sludge, organic fraction of municipal solid waste, energy crops, different waste waters from industry all serve as substrates and have different potentials for methane production.

Sewage sludge from aerobic wastewater treatment and animal manure are the most common feedstock for methane production. Methane potential of sewage sludge vary

from 200 l CH_4 / kg VS to 450 depending on the type of sewage sludge. Pig and cattle manures methane potential varies from 100 l CH_4 / kg VS to 480 l CH_4 / kg VS. (Kahiluoto et al. 2011).

Municipal solid waste is variable feedstock in content and the methane potential varies according to where it is collected, how it is sorted and the time of the year. Methane potential can vary from 100 l CH_4 / kg VS to 480 l CH_4 / kg VS. Biomass, including grasses, straws from wheat, rice and sorghum, can be grown for feedstock for anaerobic digestion or it can be a by-product of food production. Methane yields of biomass can vary between 190 l CH_4 / kg VS and 440 l CH_4 / kg VS. Fruit and vegetable wastes are easily degraded in anaerobic digestion and produce 190 l CH_4 / kg VS to 470 l CH_4 / kg VS. (Ward et al. 2008)

2.1.1 Lipids

Waste containing high amounts of lipids is produced in high amounts from slaughterhouses, oil industry and food industry etc. (Cirne et al. 2007). Theoretical methane potential of lipids is the highest of all feedstock that can be used in anaerobic digestion, but there are some limits concerning lipid usage for methane production.

Lipids can cause practical problems in anaerobic digestion operations by clogging, flotation and washouts and they can be inhibitory to anaerobic digestion process itself (Pereira et al. 2004). Fats may solidify in low temperatures and cause clogging. They can also have a low biodegradability coefficient. Part of the clogging and biodegradability issues can be overcome by treating the fat containing feedstock with lipases to partially degrade the fats and to improve the anaerobic digestion step (Cammarota et al. 2001).

Lipids are hydrolyzed to glycerol and free LCFAs in anaerobic process. Hydroxylation of lipids is catalyzed by extracellular lipases that are secreted by the acidogenic bacteria. Glycerol is converted to acetate by acidogenesis and LCFAs are converted to acetate or propionate and hydrogen through β-oxidation pathway. This is dependent on the hydrogenotrophic methanogens to use the hydrogen produced during fatty acid oxidation. (Cirne et al. 2007)

It has been postulated that LCFA are acutely toxic to the microorganisms in the β-oxidation and methanogenic pathways. According to Angelidaki & Ahring (1992) even low concentrations of LCFAs oleate and strearate inhibit all steps of the anaerobic thermophilic digestion. The lag phase of anaerobic digestion increased with the increasing concentrations of LCFAs and finally no growth was observed with high enough concentrations. The inhibition of high concentrations was permanent and the adaptation of the cultures to fatty acids did not take place. (Angelidaki & Ahring 1992) Broughton et al. (1998) tested anaerobic batch digestion of sheep tallow at levels up to 59% of VS

in mesophilic and thermophilic conditions. They were able to completely degrade the tallow in mesophilic conditions, but not in thermophilic conditions. Methanogenesis was delayed by characteristic adaptation periods before LCFAs and volatile fatty acids (VFA) were completely degraded. They concluded that methanogenesis of high lipid content requires an adaptation period in mesophilic conditions and that thermophilic microbes might be more sensitive to high lipid content. Pereira et al. (2005) were able to show by studying the biodegradation of oleic and palmitic acids that the inhibition of methanogenesis is more due to physical transportation limitations than metabolic functions and that it is reversible. Cirne et al. (2007) studied further the effect of lipid concentration on hydrolysis and methanogenesis with lipid-rich model waste. They tested different concentrations of lipids ranging from 5% to 47% w/w (chemical oxygen demand COD basis) for hydrolysis and methane production. Methane production rate was similar for concentrations 5%, 10% and 18%. Slightly stronger inhibition was observed with higher lipid concentration of 31% and 40%. The lag phase for methane production in all cases except the highest concentration was from 6 to 10 days. For the highest lipid concentration the lag phase was 60 days, but the process recovered. They were also able to enhance the hydrolysis of lipids with lipases. They concluded that the initial lag phase in methane production could be attributed to the rapid build-up of VFA and/or LCFA. The same conclusion of rate-limiting step was also presented by Salminen et al. (2000). According to Angelidaki et al. (1990) it is possible that addition of bentonite clay or calcium chlorite may control the LCFA toxicity.

2.2 Optimal conditions for anaerobic digestion

Several factors affect the anaerobic digestion. Temperature, pH, humidity, retention time, chemical composition of the feedstock, competition of organisms in the digester and the presence of toxins all have their impact on the production of methane.

Methane production can take place in wide range of temperatures, from 4ºC to 110 ºC. Usually anaerobic digestion is carried out in mesophilic conditions, where the temperature varies from 25 ºC to 40 ºC with optima at 35 ºC or in thermophilic conditions, where the temperature varies from 50 ºC to 65 ºC with optima at 55 ºC. (Bitton 2005, Ward et al. 2008) Because microbial communities active in different temperatures are very different, even small changes in temperatures can cause reduction of biogas production (Chae et al. 2008).

Methanogens and acidogenic bacteria function best in slightly different pH. For methanogens the pH optima is around 7.0 but for acidogenic bacteria and hydrolysis the pH optima is between pH 5.5 and 6.5. The production of organic acids by acidogens lowers the pH of the process and under normal conditions, it is buffered by methanogens producing biocarbonate. The pH value increases by ammonia accumulation when proteins

are degraded. If the pH falls too low and buffering capacity is not working, the methane production can be disrupted. The optimal pH for the reaction should be in the range of 6.8-7.2 (Bitton 2005, Ward et al. 2008, Weiland 2010).

The retention time (HRT) has to be long enough to allow sufficient time for the metabolism of anaerobic microbe in digester. The HRT can vary between 25 to 35 days but it can be also longer (Bitton 2005).

Chemical composition affects the production of methane. It can be produced from carbohydrates, proteins, lipids and from complex aromatic compounds, but some compounds like lignin are less degraded in the process. Process has to contain balanced carbon, nitrogen, phosphorus and sulfur concentration to allow the methane production. The C:N:P ratio of 700:5:1 for anaerobic bacteria is ideal, also the C/N ratio of 25-30:1 for biogas production is working. Also some trace elements, such as iron, cobolt, molybdenum, nickel, selenium and tungsten are needed and need to be added if the feedstock does not contain them in sufficient amounts. (Bitton 2005, Weiland 2010).

There are many inhibitory toxics that may influence the performance of anaerobic digestion. Oxygen is toxic to methanogens that are obligate anaerobes. Un-ionized ammonia (NH_3) inhibits methanogenesis. Ammonia is produced when nitrogenous matter, such as proteins are degraded. Concentration, pH, temperature, presence of other ions and acclimation all contribute to the degree of ammonia inhibition. Sulfide is formed when sulfate which is a common constituent of industrial wastewaters is reduces by sulfate reducing bacteria (SRB). Sulfate reduction leads to two types of inhibition. Primary inhibition is caused by the competitions for common organic and inorganic substrates from SRB, which suppresses the methane production. Secondary inhibition is due to the toxicity of sulfide to various bacteria groups. Light metals ions (Na, K, Mg, Ca and Al), heavy metals and organics like chlorophenols, halogenated aliphatics N-substituted aromatic and LCFAs all have toxic effects to the process in certain conditions. (Bitton 2005, Chen et al. 2008). Inhibitory effects of LCFAs have been discussed in previous chapter.

2.3 Pretreatment methods for enhancing biomethane production

There are multiple ways to pretreat and enhance biomethane production in anaerobic digestion process. These pretreatment methods include thermal treatment, chemical treatment with alkali, milling, ultrasonication, ozonation, biological methods and adding additives and nutrients. Efficacy of different methods is dependent on the material treated. The aim of pretreatment is to shorten the stabilization time, increase the biodegradation efficiency and improve the biogas production by increasing the hydrolysis and availability of organic wastes.

2.3.1 Temperature

In thermal pretreatment of anaerobic digestion feedstock elevated temperatures in the range of 60-200ºC can be used. Thermal treatment process is often performed in pressure ranging from 600-2500 kPa. Effectiveness of thermal treatment is dependent on the feedstock treated. (Appels et al. 2008). Thermal pretreatment has been studied especially for waste-activated sludge (WAS), food waste, agricultural byproducts, pig slurry and cattle and swine manure while few studies on solid waste has published.

For WAS maximum increase in gas production at 60 ºC and maximum VS reduction at 100 ºC was shown by Hiraoka et al. (1989). 60% increase in soluble COD in 170 ºC after one hour treatment of WAS, but also loss of total COD was observed in high temperatures. Biodegradability improved by 45% with one hour thermal pretreatment at 170 ºC in batch test. In continuous anaerobic digestion reactor the increase in biogas production improved by 54%, COD degradation by 71% and total solids (TS) degradation by 59%. (Valo et al. 2004)

Treatment of food waste at 150 ºC for one hour was more efficient than treatment at 70 ºC for two hours. Biogas production increased by 8% and 1%, VS removal increased by 4% and 2% and COD removal increased by 5% and 3% respectively. Most significant finding was that the use of thermally pretreated food waste halved the time to produce the same quantity of methane in comparison with anaerobic digestion of fresh food waste (Wang et al. 2006).

The effect of particle size and thermal pretreatment on the methane yield of four different byproducts of agriculture was investigated by Menardo et al. (2012). Wheat, barley, rice straw and maize stalks were pretreated at 90 ºC or 120 ºC in autoclave. Thermally-pretreated maize stalks and rice straw showed no statistically significant improvement in the methane yields. Barley and wheat straws were influenced by thermal treatments and the methane yield increased significantly, around 40% and 60% respectively. (Menardo et al. 2012).

The solid fraction of mixed cattle and swine manure was heated to 100-140 ºC. This improved the methane production and increased the VS removal (Mladenovska et al. 2006).

2.3.2 Alkaline treatment

Alkaline pretreatment of anaerobic digestion feedstock can be performed with different alkali, like calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH) or potassium hydroxide (KOH). The aim of alkali treatment is to increase the biodegradability of the feedstock, thru solubilization and/or disintegration of the feedstock like lignin.

The influence of 6% NaOH pretreatment for biogas production when rice straw was used as feedstock for anaerobic digestion was studied by He et al. (2008). They showed 27-64% increase in the production of biogas compared to untreated feedstock. Degradation of 16% cellulose, 37% hemicellulose and 28% lignin were observed and water-soluble substances were increased by 122%. Linkages of lignin, hemicellulose and cellulose were broken or destroyed, leading to significant changes in chemical structure. They were able to conclude that the alkaline treatment changed the chemical composition, structure and physical characteristics of rice straw and made it more available and biodegradable and therefore increased the biogas yield. (He et al. 2008)

Corn stover was treated with different amounts of NaOH. The lignin degradation increased during pretreatment from 9.1% to 46.2% when NaOH concentration was increased from 1.0% to 7.5%. The highest increase in the biogas production was obtained with 5% NaOH. Compared to untreated corn stover, the NaOH treatment increased the biogas production by 37%. (Zhu et al. 2010)

Kraft mill sludge was solubilized with NaOH or KOH with doses from 20 to 200 mEq/l. Up to 32% increase was obtained in the soluble COD/ total COD ratio with 80 mEq/l dose. The methane production potential was not tested in this study. (Navia et al. (2002). Valo et al. (2004) were also able to increase the COD solubilization of WAS from 3% to 30% , but they concluded that most of the solubilized matter was from mineral and KOH added. They also showed no statistically significant increase of biogas production compared to raw sludge. They concluded that this was due to two different reasons: inhibition of methanization by refractory molecules solubilized by the base or too small a quantity of organic matter solubilized to see a real difference with raw WAS digestion.

Lopez Torres et al. (2008) studied the effect of alkaline treatment with $Ca(OH)_2$ to the organic fraction of municipal solid waste (OFMSW). The organic material is complex and it needs to be broken into simple monomers, to increase the solubilization of organ-

ic material (sCOD) and thereafter to improve the efficiency of anaerobic treatment. They were able to solubilize 11.5% of COD and produce 172% methane compared to control when OFMSW was treated with 62.0 mEq/l of $Ca(OH)_2$ for 6 hours.

3 BLEACHING EARTH

There are two basic types of commercially available bleaching earth (clays), natural and activated bleaching earth. The activated bleaching earth is mostly used, as it has a higher adsorption capacity. Bleaching earth activation by acid, alkaline or organic are used to enhance and alter the properties of clays to suit in different adsorption processes. Changes in the specific surface area size and pore volume effects the adsorption capacity of metal impurities, phosphatides and color bodies. The relationship between porous morphology and surface chemistry has an important effect in bleaching earth performance. (Hussin et al. 2011).

3.1 Clays

The physical and chemical properties of different clays depend on their structure and composition. There are different molecular structures of clay minerals (Figure 3.1, Table 3.1).

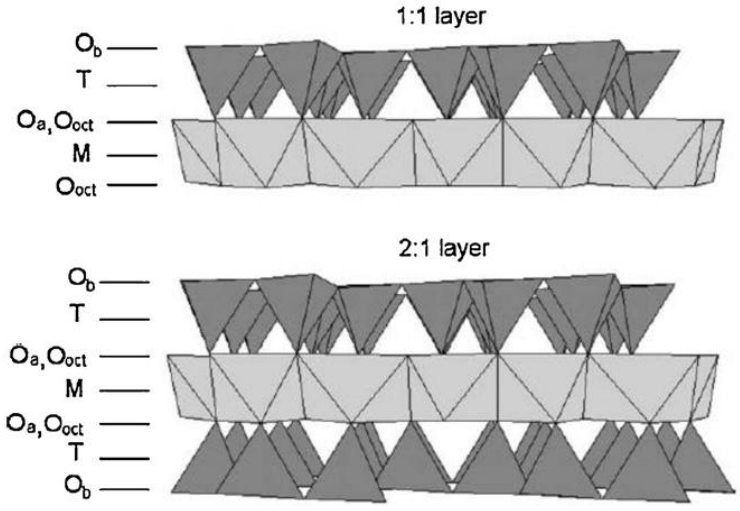


Figure 3.1Layer types 1:1 and 2:1of clay mineral structure. Oa, Ob, Ooct refer to tetrahedral basal, tetrahedral apical and octahedral anionic position, respectively. M and T indicate the octahedral and tetrahedral cation, respectively. (Bergaya et al. 2006).

In 1:1 layer type, one octahedral sheet is linked to one tetrahedral sheet. Kaolins and serpentines have this layer type. Kaolinite, dickite, nacrite, halloysite, chrysolite, lizardite and amesite belong to these groups, kaolinite being the most common mineral. 2:1 layer type consists of two tetrahedral sheets sandwiching on octahedral sheet. Smectine has 2:1 layer type. The smectine group consists of several clay minerals, but sodium montmorillonites are the most important industrial clay minerals in this group. Palygorskite has an inverted 2:1 layer type. They are hydrated magnesium aluminum silicate minerals. (Hussin et al. 2011, Murray 2000).

Table 3.1 Clay mineral properties and applications (adapted from Hussin et al. 2011 and Murray 2000)

Kaolin	*Smectine*	*Palygorskite*
Clay mineral properties		
1:1 layer	2:1 layer	2:1 layer inverted
White or near white	Tan, olive green, gray, or white	Light tan or gray
Little substitutions	Octahedral and tetrahedral substitutions	Octahedral substitutions
Minimal layer charge	High layer charge	Moderate layer charge
Low base exchange capacity	High base exchange capacity	Moderate base exchange capacity
Pseudo-hexagonal flakes	Thin flakes and laths	Elongate
Low surface area	Very high surface area	High surface area
Very low absorption capacity	High absorption capacity	High absorption capacity
Low viscosity	Very high viscosity	High viscosity
Applications		
Paper coating	Drilling mud	Drilling fluids
Paper filling	Foundry bond clay	Paint
Paint extender	Pelletizing iron ores	Agricultural carriers
Ceramic ingredient	Sealants	Industrial floor absorbents
Rubber filler	Animal feed bonds	Bleaching clay
Plastic filler	Bleaching clay	Tape joint compounds
Ink extender	Agricultural carriers	Cat box absorbents
Cracking catalysts	Adhesives	Suspension fertilizers
Fiberglass	Pharmaceuticals	Animal feed bondants
Cement	Emulsion stabilizers	Catalyst supports
Adhesives	Desiccants	Adhesives
Enamels	Cosmetics	Paper
Pharmaceuticals	Paint	Pharmaceuticals
Crayons		Anti-caking agent
Molecular sieves		Reinforcing fillers
		Environmental absorbents

Industrial use of clay minerals is dependent on their properties: particle size, shape, distribution and surface chemistry, area and charge (Table 3.1). For example kaolins are used in paper coating and paint applications due to their relatively low viscosity. Also ceramics, like whiteware, sanitaryware, insulators and pottery are important traditional usage of kaolins. (Murray 2000)

Smectines, namely calcium and sodium montmorillonates, most commonly occur in bentonite, a clay altered from glassy ingenous material. Sodium montmorillonate is used in fresh water drilling muds. Calcium montrorillonate is used for decolorization of vegetable, animal and mineral oils. (Murray 2000) Mostly acid activated calcium bentonite is used for filtering and decolorizing oils (Odom 1984).

3.2 Utilization of spent bleaching earth

SBE can contain oils, fats, colored pigments, metal traces, etc. depending on the purpose it was used and the technology applied (Chang et al. 2006). Around 2 million tons of spent bleaching earth is produced world-wide annually. Not many possibilities for beneficial reuse of the material exist, but many ideas have been presented, mostly in smaller scale (Beshara & Cheeseman 2014). It would be beneficial to be able to reuse, recycle or use as energy source SBE instead of dumping it to landfills or incinerating it. It is possible to use SBE as addition to animal feed, incineration, in cement and in brick production, for soil improvement and composting, feed stock for biogas production and for extraction and regeneration.

There are several parameters that affect the disposal, storage and transport of SBE: tendency to self-ignition, oil and water content, biological degradation of organic components, heavy metal content and amount of non-bentonite material (activated carbon, filter aid, silica etc.). Possibilities to use SBE are affected by the type of impurities in SBE, logistics, and economical and ecological aspects. (Münch 2005)

3.2.1 Construction materials

The reuse of spent bleaching earth as novel clay blocks for construction was studied by Beshara & Cheeseman (2014). The residual organic components in SBE start to polymerize when treated with low pressure followed by heat treatment at 150^{0}C. This process produces monolithic samples with high unconfined compressive strengths.

3.2.2 Animal feed

Lye extraction, which is extraction by weak caustic solution, was used to extract the oil from the SBE. The oil content was reduced to less than 1% when boiling SBE with caustic soda solution. Chang et al. (2006) suggested to feed the remaining SBE to animals by mixing it in the soy meal for animals.

Also the use of SBE used for palm oil extraction as fish feed instead of marine fish oil that is used as main dietary lipid source in many commercial fish feeds was studied. It was concluded that palm oil SBE can totally replace fish oil in fish feed. This will help to reduce the costs of fish feed, serve as feed binder, remove mycotoxins from fish feeds and adsorb toxic substances in the culture waters (Ng et al. 2006).

3.2.3 Biodegradation

The composting properties of oiled bleaching earth (OBE) in order to find a suitable treatment method for OBE was investigated. 19% of OBE was mixed with waste sludge and maize straw as a structural material. It was shown that fatty acids biodegraded during composting by 95% and no toxic effects were seen on the mature compost. The conclusion was that the method is suitable for treating the OBE waste along with the benefit of producing fertilizer (Piotrowska-Cyplik et al. 2013).

The possibility to biodegrade SBE containing metals and heavy polycyclic aromatic hydrocarbons was studied by Kassim et al. (2013). They incubated SBE, high in organic carbon and low in nitrogen, in combination of soil micro-organisms and different levels of nitrogen. They were able to show that soil microorganisms are capable of mineralizing carbon in SBE samples and therefore remove at least some of the remaining oil in SBE.

3.2.4 Fertilizer

SBE can be used as fertilizer as well. By co-composting SBE with agricultural and palm oil milling by-products, suitable fertilizer is produced. Composted SBE has adequate amounts of beneficial mineral elements, it improves organic carbon content, cation exchange capacity, water-holding capacity and C:N ratio and therefore it has a positive impact on soil physical attributes and microbial rejuvenation. Loh et al. were able to show 50% increases in the productivity of okra, kangkung and groundnut magenta. (Loh et al. 2013).

3.2.5 Recycling – deoiling

It would be advantageous to be able to recycle the SBE. For that purpose SBE needs to be deoiled and regenerated for further use.

SBE was regenerated by pyrolysis in a rotary furnace by Tsai et al. (2002). The pyrolysis temperature of 500-600ºC was used. They were able to regenerate the SBE but the regenerated clays had smaller surface areas and pore volumes, which would affect their adsorption properties. Also the adsorbed oil is lost during pyrolysis.

SBE regeneration by thermal treatment at 500 ºC, one hour carbonization time followed with 1 M hydrochloric acid wash was studied (Boukerroui & Ouali 2000). The resultant regenerated bleaching oil showed similar adsorption properties as did a commercial virgin bleaching earth.

The heat and acid reactivation of SBE and adsorption of Cu(II) ions from aqueous solutions was investigated by Wambu et al. (2009). Solvent extraction of residual oil with methylethyl ketone followed with heating at 370 ºC, was the most efficient method for reactivation in their study. The adsorption capacity of over 90% was regenerated when analyzed using Cu(II) ions making it possible to reuse the bleaching earth for its original purpose.

Regeneration of SBE can be achieved by treating SBE with an aqueous cetyltrimethylammonium bromide solution to remove the edible oil impregnating the solid material and to intercalate the ammonium cation in the interlayer space of the bentonite. According to dye removal experiments performed, the regenerated sorbent performed better than some of nonconventional sorbents. (Mana et al. 2011)

3.2.6 Fuel briquette

The possibility to prepare SBE briquettes for fuel purposes was studied by Suhartini et al. (2011). They added different concentrations of maltodextrin and different pressure to SBE in order to produce briquettes. Their conclusion was that it is feasible to use SBE waste as feedstock in briquetting. Different conditions has effect on the water content, combustion rate, compressive strength and product yield but they did not have significant effect for caloric value and combustion ashes. (Suhartini et al. 2011)

3.2.7 Biodiesel

Biodiesel was produced by lipase-catalyzed methanolysis. SBE from crude vegetable oil refining process was used. The SBE contained 40% of its weight as oil. The oils

were organic-solvent extracted and identified as soybean, palm and rapeseed oil. Rhizopus oryzae lipase was able to catalyze the methanolysis of extracted oils to produce biodiesel. (Lara Pizarro et al. 2002)

The technical and economic feasibility of producing biodiesel from the residual oils recovered from SBE were studied by Huang & Chang (2010). They were able to produce biodiesel with a quality in reasonable agreement with EN 14214 and ASTM D6751 standards. The financial analysis showed that investment to this kind of process would be most beneficial when the crude oil price is high.

3.2.8 Biogas production

Few studies of using SBE as feedstock for biogas production have been published. Campos et al. (2000) studied the codigestion of pig slurry with olive bleaching earth (OBE) intending to improve the methane production from pig slurry, which methane potential is relatively low. Addition of 5% and 12.5% of OBE in batch experiment resulted in increase of methane yield compared to pig slurry alone. However the lag phase increased with the increasing cosubstrate fraction. Maximun yield was achieved with 5% OBE. They showed the accumulation of VFA with 12.5% OBE and concluded that accumulation of LCFAs inhibited the process.

The potential of codigestion of SBE from Omega 3 oil refining industry with animal manure was studied by Ward (2012). Cattle manure with 2.5% to 12.5% SBE to study the methane potential was used. The observation was that methane yield decreased with increasing portion of SBE in the substrate. The methane production varied from 327 l/kg VS to 278 l/kg VS optimum being 7.5% SBE added. The lowest yield as l/kgVS was obtained when 12.5% SBE with cattle manure was used. The highest methane yield per wet weight, was obtained with 10% SBE (ww) and decrease was seen when 12.5% SBE (ww) was added suggesting inhibition. The biogas produced contained 65-67% methane. The conclusion of the study was that even though the overall production of methane in terms of VS is decreases, the yield in terms of wet weight is increased because the high energy-density of SBE, and therefore it would be beneficial for the biogas facility to add SBE to the feedstock. Adding 10% (ww) SBE into to the feedstock would increase the volumetric methane production by 35%.

The solid-state anaerobic codigestion of hay and soybean processing waste (SPW) for biogas production was studied by Zhu et al. (2014). SPW consisted of soybean straw, beans, soybean oil residue, and diatomaceous earth used in bleaching process. The protein content of SPW is high, so it was codigested with hay to balance the C/N ratio and to improve the methane yield. The increase in the methane yield by codigestion was shown in the study.

Biogas facilities using SBE as feedstock for methane production exists. The Scherbring GmbH biogas plant in Germany uses a variety of substrates, including pig manure, bleaching earth, dog food, fatty wastes, potatoes etc. Pig manure and bleaching earth are the dominant feedstock. In the year 2008 5500 tons of bleaching earth was used, the total amount of feedstock being 28000 tons per year. Also in Germany, the Biogas plant Wietmarschen (EU-AGRO-BIOGAS, 2010) and Lemvik Biogas in Denmark take in bleaching earth to be used as feedstock for anaerobic digestion process to produce biogas. (Lemvik biogas)

4 MATERIALS AND METHODS

4.1 Substrate and inoculum

Oil-clay mixture used in the study is a by-product of oil refinery industry. Also unused clay was available.

As inoculum three different sludges were used for methane potential production assays. Mesophilic inoculum 1 (Forssa, Finland) was from biogas production facility where agricultural and industrial by-products together with sewage sludge are used to produce biogas. Mesophilic inoculum 2 (Kouvola, Finland) is from biogas production facility using sewage sludge, biowaste and silage. Thermophilic inoculum (Turku, Finland) is from biogas production facility using sewage sludge as feedstock to anaerobic digestion at 55C.

4.2 Alkaline and thermal pretreatment of oil-clay

First batch of oil-clay were treated with different amounts of alkali (NaOH) overnight either shaking or in steady conditions in order to see if the availability of the substrate would increase. In low volume solubilization test, 20 g of oil-clay sample was suspended to 40 ml of 0.25 M, 0.5 M, 1.0 M, 1.5 M or 2.0 M NaOH. Second batch of oil-clay were treated with alkali overnight by adding 500 ml of 0.1 M, 0.25M, 0.5M, 1.0M or 1.5M NaOH to 5 g of oil-clay sample (high volume solubilization). SCOD analyses were performed the following day for all samples.

Thermal pretreatment for oil-clay samples were performed in 25 ºC, 37 ºC, 55 ºC and 70 ºC for 24 hours. 5g of oil-clay sample was suspended to 500 ml MilliQ water. The samples for SCOD analyses were taken from the liquid phase of mix and not filtered to avoid the attachment of oil to the filter.

4.3 Methane potential assays

Methane potential test was based on the method developed by Hansen et al. (2004). The test was carried out as triplicate batch experiments using 120 ml glass serum bottles with gas tight rubber septum. Inoculum/substrate VS-ratio of 1:1 was used. Substrate containing 0.3 g of VS was added to each bottle. One batch included substrate treated

overnight with 1 M NaOH (2.7% ww NaOH, low volume method). To deduct the baseline methane production of inoculum only, no substrate was added to one set of bottles for each inoculum used. 25 ml of MilliQ water was added to bottles, pH adjusted between 7 and 8, salts (NH_4Cl, 0.3 g/l; NaCl, 0.3 g/l; $CaCl_2 \cdot 2H_2O$, 0.1 g/l and $MgCl_2 \cdot 6H_2O$, 0.1 g/l) and buffer ($NaHCO_3$, 4 g/l) added. Liquid volume was adjusted to 60 ml with milliQ after the addition of appropriate amount of inoculum. Bottles were flushed with N_2 and 0.2 ml 0,1M Na_2S was added to each bottle to remove the oxygen from the bottles. Bottles were placed to water bath of 35-37ºC when mesophilic inoculum was used and to 55 ºC when thermophilic inoculum was used. Different inoculum substrate combinations tested are listed in Table 4.1 Thermophilic and mesophilic 1 batch tests were performed simultaneously and mesophilic 2 batch test on separate run.

Table 4.1 Methane production batch tests: inoculum and substrates used.

Inoculum	**Substrate**
Thermophilic	Oil-clay
	Alkaline treated oil-clay
Mesophilic 1	Oil-clay
	Alkaline treated oil-clay
Mesophilic 2	Oil-clay
	Unused clay

4.4 Settling experiments

Settleability of oil-clay sample was studied by observing the settleability of the sample in Imhoff cone. 5 and 10 g of oil-clay sample were used with 1000 ml of tap water. The pH of the mixture was either adjusted to pH 7-8 or not adjusted. In another part of the experiments vertical mixer was used to study if it was possible to mix the floating oil-clay. Settling volume was calculated as volume of settled material (ml)/g TS sample. 500 ml of tap water and 20 g of oil-clay were put into stirring vessel and stirred overnight with 10, 20, 30 or 40 rpm. Observations of settling or floating were made and recorded the following morning.

4.5 Analyses

Analyses performed included pH measurements, total solids (TS) and volatile solids (VS) analyses, SCOD, volatile fatty acids (VFA), total nitrogen measurement and settleability.

TS and VS were determined for the samples, substrates and sludges, according to SFS 3008 standard. Scaltec SBC31 scale (Denver Instrument, Germany) was used for weighing and Memmert heating oven (Memmert GmbH + Co.KG, Germany) for 105ºC and Heraeus furnace (Thermo Scientific, USA) for 550 ºC.

pH was measured with WTW pH3210 pH-meter (Weilheim, Hermany). Oil-clay and unused clay were first suspended to milliQ water, incubated from 1h to 24 hours and measurement performed from the liquid phase.

SCOD was analyzed with a method based on standard SFS 5504. Oil-clay and unused clay were suspended in MilliQ water overnight. All samples to be analyzed for sCOD were either centrifuged 5000g 30 minutes (Sigma 4K15, B.Braun Biotech International) and filtered thru GFA filter (Whatmann, GE Healtcare) or just filtered prior to analyses.

VFAs were analyzed from oil-clay samples. Oil-clay was treated as in SCOD analyses and filtered through 0.45 µm filter and frozen.

Total nitrogen content of the oil-clay sample was measured with Kjeldahl nitrogen determination method based on standard EN 16169. Kjeltabs (Foss, Denmark) were used as catalyst mix with 12 ml of sulfuric acid. Digestion was performed for 1 hour in 200 ºC and 1 hour in 370 ºC using Tecator Digestor (Foss, Denmark).

Methane production in each bottle was followed regularly by measuring gas samples with gas chromatography (GC), Shimadzu GC-2014 (Shimadzu Corporation, Japan) using TCD detection and packed column Poropak N80 (Agilent Technologies, USA). Gas samples were taken from the head space of the bottles and injected to GC with pressure lock syringe (Hamilton Company, USA). As carrier gas N_2 (flow 20 ml/min) was used, with following parameters: injector 110 ºC, column 80 ºC, detector 110 ºC. Methane volumes are normalized to standard conditions (1 bar pressure, 273K temperature) when presented in this work. The pressure from the bottles was released as needed and the released amount was taken into account in the calculations.

5 RESULTS

5.1 Characterization of samples

TS, VS, pH, SCOD, N and VFA were determined for oil-clay and unused clay samples (Table 5.1). TS content of oil-clay was 98.1% while TS for unused clay was only 64%. VS contents were 43.1% and 2.8% respectively. Both oil-clay and unused clay were acidic (pH 3.5 and 3.2) in water suspensions. Soluble COD of oil-clay in water suspension was 41.9 mg/g. The nitrogen content was 0.2%. No VFA was found when the original oil-clay sample was analyzed.

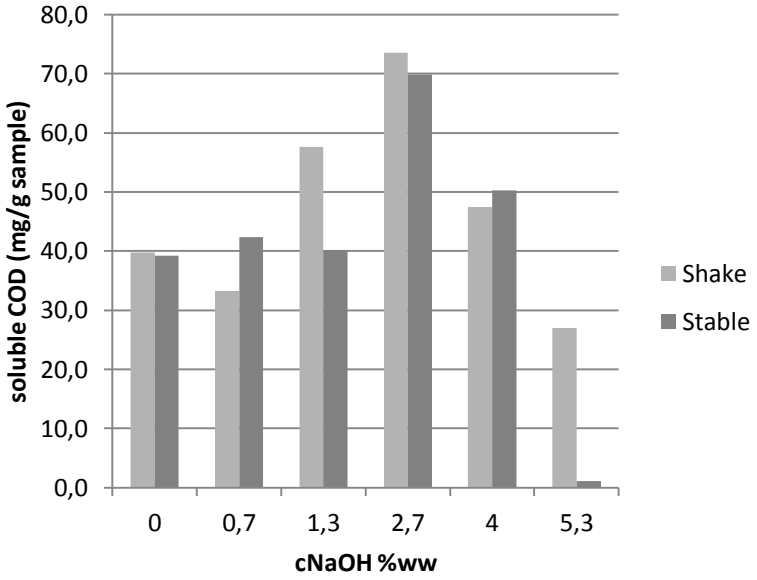
Table 5.1 TS, VS, pH, SCOD and N of oil-clay and unused clay samples.

Sample	TS (% ww)	VS (% ww)	pH	SCOD (mg/g sample)	N (% TS)
Oil-clay	98.1	43.1	3.5	41.9	0.2
Unused clay	64.0	2.8	3.2	0.025	na.

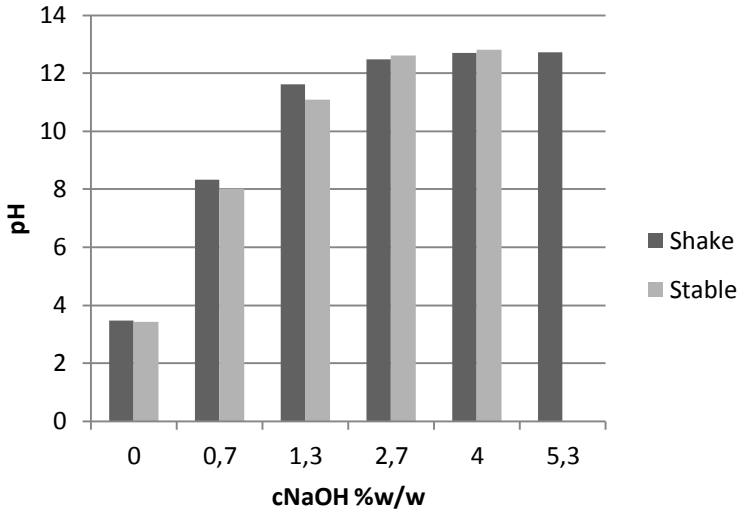
5.2 Alkaline pretreatment of oil-clay sample

Alkaline pretreatment in order to release oil from clay into liquid phase was performed with different concentrations of NaOH (Figure 5.1). Highest soluble COD amount of 74 mg/g sample was measured after treatment of oil-clay with 2.7% NaOH in batch 1 and amount of 320 mg/g sample with 1% NaOH in batch 2. pH was over 12 in batch 1 with 2.7% NaOH and over 12 in all samples in batch 2.

a.



b.



c.

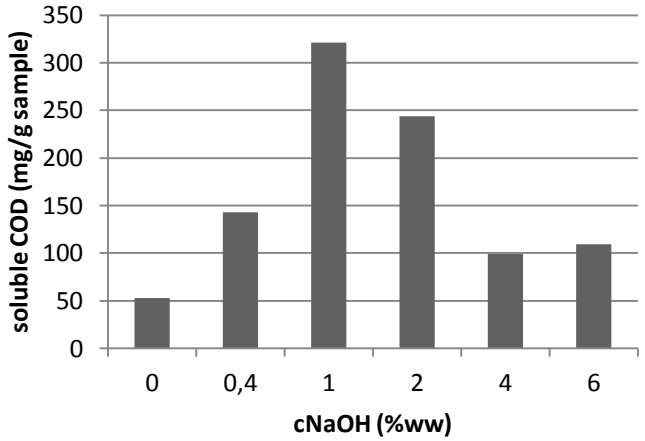


Figure 5.1 Effect of alkaline treatment on SCOD. a) Batch 1: Liquid to sample ratio of 2:1. b) pH at different NaOH concentrations. Batch 1.c)Batch 2. Liquid to sample ratio of 100:1.

5.3 Thermal pretreatment of oil-clay sample

Different temperatures (20, 37, 55 and 70 ºC) were used to study the effects of thermal treatment of oil-clay to release oil from clay (Figure 5.2). pH in all samples used was below 4. No increase in SCOD was observed as the SCOD was between 48-54 mg/g in all samples.

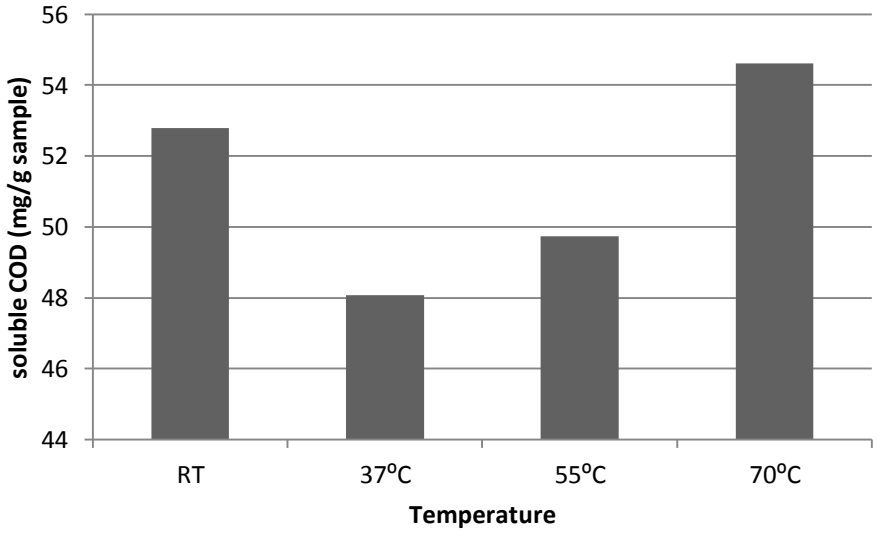


Figure 5.2 Effect of thermal treatment to SCOD.

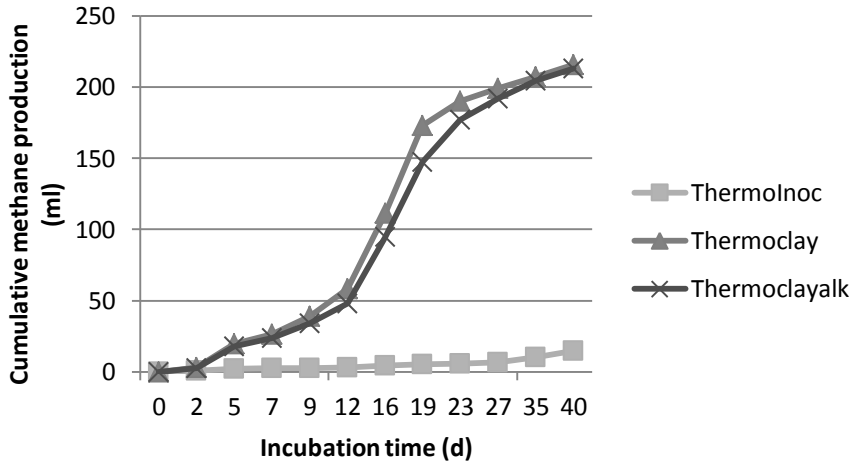
5.4 Methane potential of oil-clay substrate

Methane potential assay was run in thermophilic and mesophilic conditions. Thermophilic and mesophilic 1 assays show similar cumulative methane production in 40 days (Figure 5.3). When using oil-clay as substrate mesophilic 1 production initiated faster, while thermophilic production started later but continued longer. The overall production was over 200ml in both. The alkaline treated oil-clay behaved similarly and there were no advantage or disadvantage of using alkaline pretreatment. With mesophilic 2 inoculum and oil-clay substrate the methane production started only after ten days, but reached almost 250 ml in 28 days. When unused clay was used as substrate methane production was below the methane production from inoculum only.

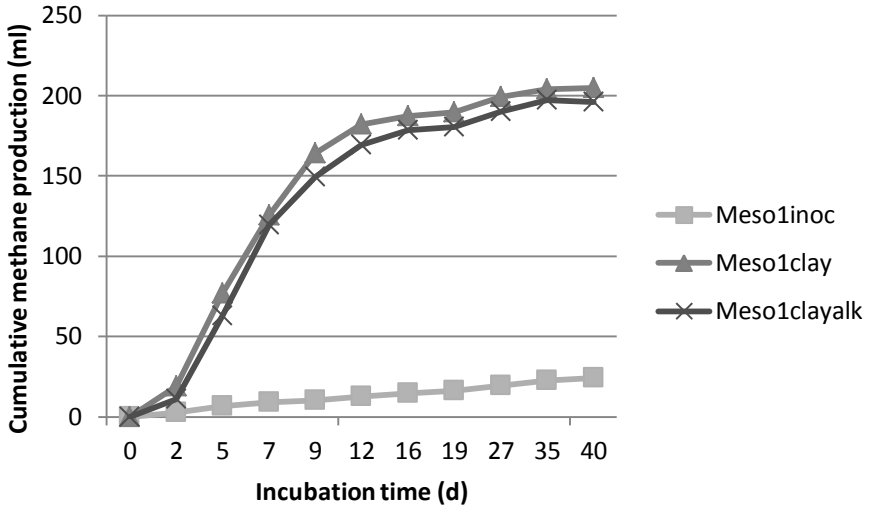
Cumulative methane production (

Figure 5.4) per substrate VS added, reached over 600 l CH_4/kg VS added when mesophilic 2 inoculum was used. With mesophilic 1 and thermophilic inoculum the production was slightly lower, but no statistical difference is shown.

a.



b.



c.

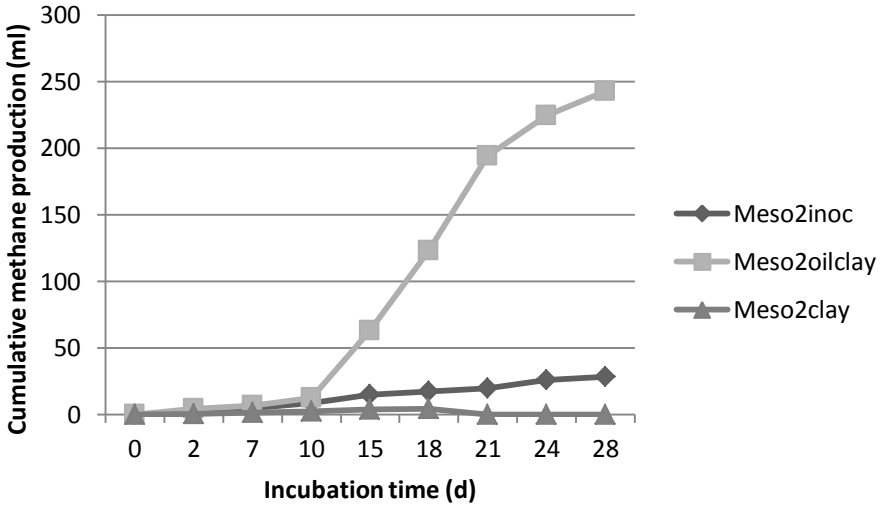
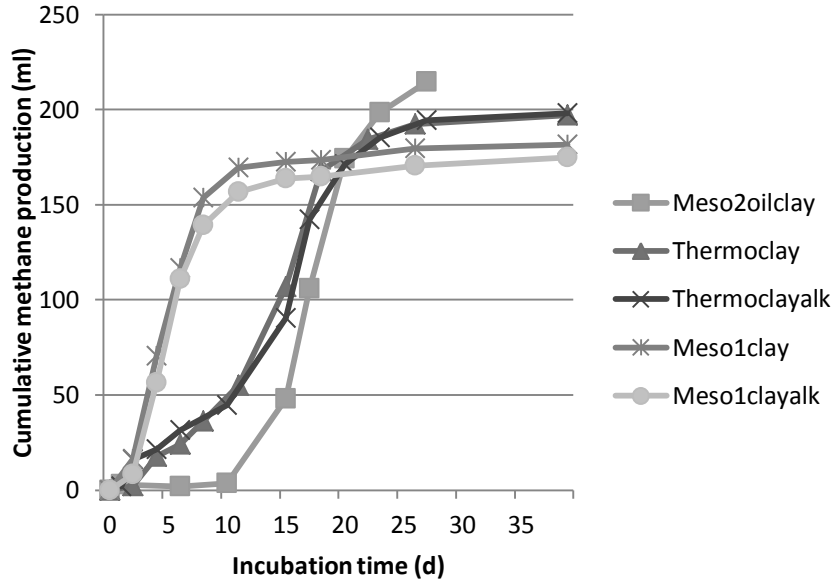


Figure 5.3 Cumulative methane production (ml) from clay with thermophilic inoculum (a), mesophilic inoculum 1 (b) and mesophilic inoculum 2 (c). Methane production of

inoculum only is not reduced as the methane production from inoculum is shown in the figures.

a.



b.

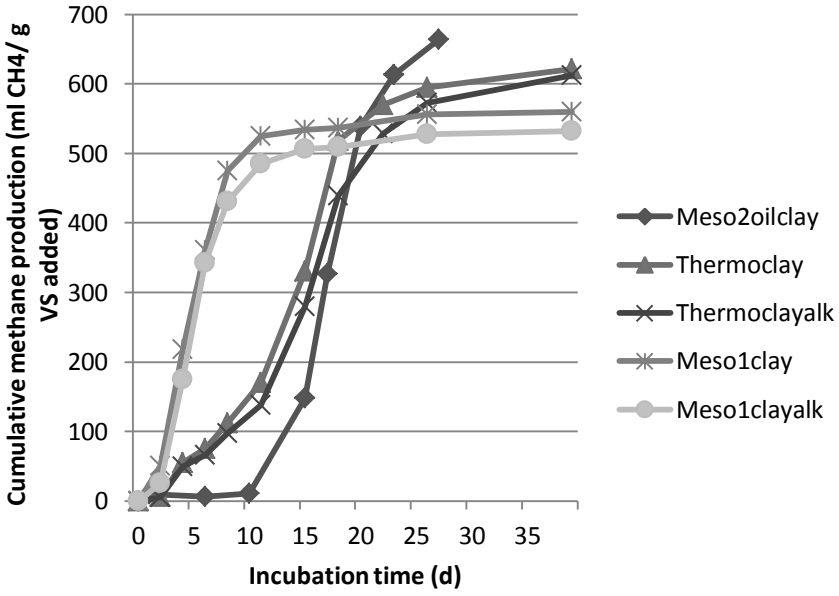


Figure 5.4 Cumulative methane production of substrates. a) Cumulative methane production per substrate (ml CH_4), inoculum production subtracted. b) Cumulative methane production per added substrate VS (ml CH_4/g VS added). Methane produced with inoculum subtracted.

Digestate characteristics after methane potential assay were studied (Table 5.2.). Substrate VS removal from 65 to 77% was achieved with all oil-clay substrates. TS removal varied from 20 to 48%. TS removal was smaller in alkaline treated samples, due to the fact that initial TS values are calculatory and does not include the chemicals added, while the digestate values are analyzed directly from the assay bottles. Cumulative CH_4 production / kg substrate VS added varies from 532 l to 663 l, alkaline treated oil-clay with mesophilic inoculum 1 being the lowest and oil-clay mesophilic inoculum 2 the highest. Cumulative CH_4 production / kg substrate VS removed varied from 728 l to 922 l being lowest in mesophilic 1 oil-clay assay and highest in thermophilic alkaline treated oil-clay assay. SCOD values in digestates range from 0.4 to 2.8 g/l. There are no differences between inoculum and corresponding substrate containing assays. Final pH of all assays was between 7 and 8, except in thermophilic inoculum (pH 8.2).

Table 5.2 Digestate characteristics after methane potential assay including methane production results.

	Mesophilic 1			Mesophilic 2		Thermophilic		
	Inoculum	Oil-Clay	Alk.treat. Oil-Clay	Inoculum	Oil-Clay	Inoculum	Oil-Clay	Alk.treat. Oil-Clay
TS (%)	1,0	2,0	2,3	1,0	1,8	1,0	1,7	2,0
VS (%)	0,5	0,6	0,7	0,5	0,6	0,5	0,6	0,7
VS/TS (%)	0,5	0,3	0,3	0,5	0,4	0,5	0,4	0,3
TS-removal (%)	0,0	43,6	20,2	0,0	41,1	0,0	48,3	20,7
VS-removal (%)	0,0	77,7	66,0	0,0	70,1	0,0	76,0	65,1
CH4 produced (ml)	24,0	205,0	196,1	28,1	242,8	14,7	215,8	212,9
L CH4/kg substrate VS added	-	559,5	532,1	-	663,7	-	621,5	612,5
L CH4/kg substrate VS removed	-	727,8	816,4	-	865,0	-	834,0	921,6
SCOD (g/l)	0,4	0,5	0,6	2,4	1,7	2,9	2,6	2,8
pH	7,7	7,2	7,3	7,8	7,3	8,2	7,8	7,8

In Figure 5.5 cumulative production of biogas, including CH_4 and CO_2 is presented. At the end the methane content of biogas is around 76%.

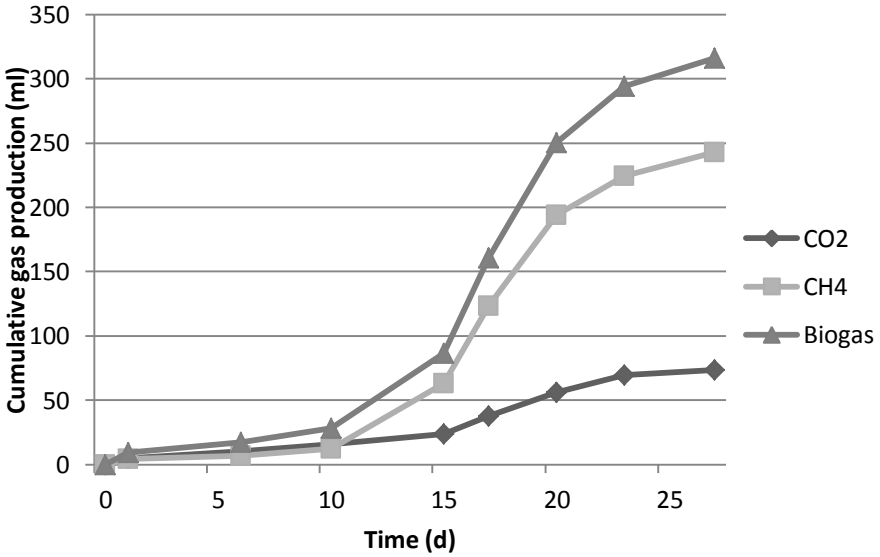


Figure 5.5 Cumulative biogas, CH_4 and CO_2 production from oil-clay with mesophilic 2 inoculum.

5.5 Settling experiments

Settling experiments were run in two different setting, with Imhoff cone and with mixing apparatus. Adjusting pH or different amounts of sample had no effect on the settleability of the oil-clay sample (Figure 5.6). Only mixing the sample prior or during settling allowed the sample to settle at the bottom of the cone. In this case premixing with water for 20-25 minutes was sufficient for efficient settling. Settling volume of around 3 ml/g was obtained in all mixed experiments while without premixing the oil-clay did not start to settle.

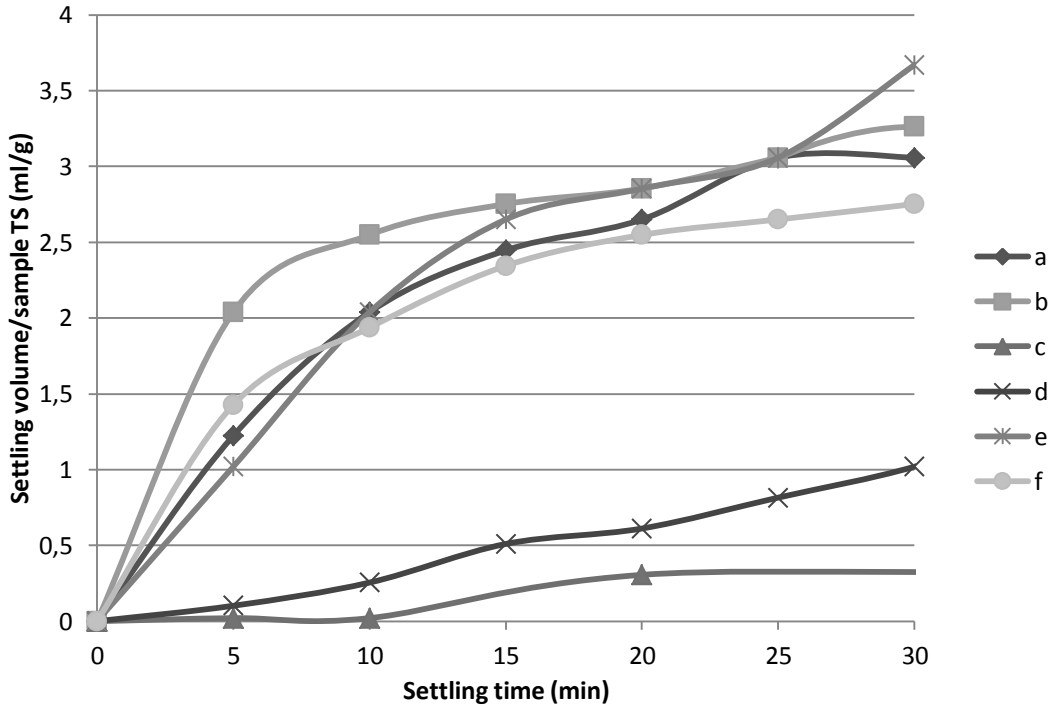


Figure 5.6 Settling experiment with Imhoff cone. Settling of oil-clay expressed as Settling volume/sample TS (ml/g). a) Settling with premix, no pH adjustment, 5g sample. b)Settling with premix, no pH adjustment, 10g sample. c) Settling without premix, no pH adjustment, 5g sample. d) Settling without premix, no pH adjustment, 10g sample. e) Settling with premix, pH adjustment to 8, 5g sample. f) Settling with premix, pH adjustment to 8, 10g sample.

Settling properties were followed in vertical stirrer (Figure 5.7). Oil-clay has a tendency to stick to the plastic stirrer. It also floated as long as it is properly stirred, after which it settled to the bottom of the vessel. By increasing stirring speed it was possible to control settleability of the oil-clay (figure 5.7b). With highest speed used, 40 rpm, oil-clay settled more than with the lower speed vessels.

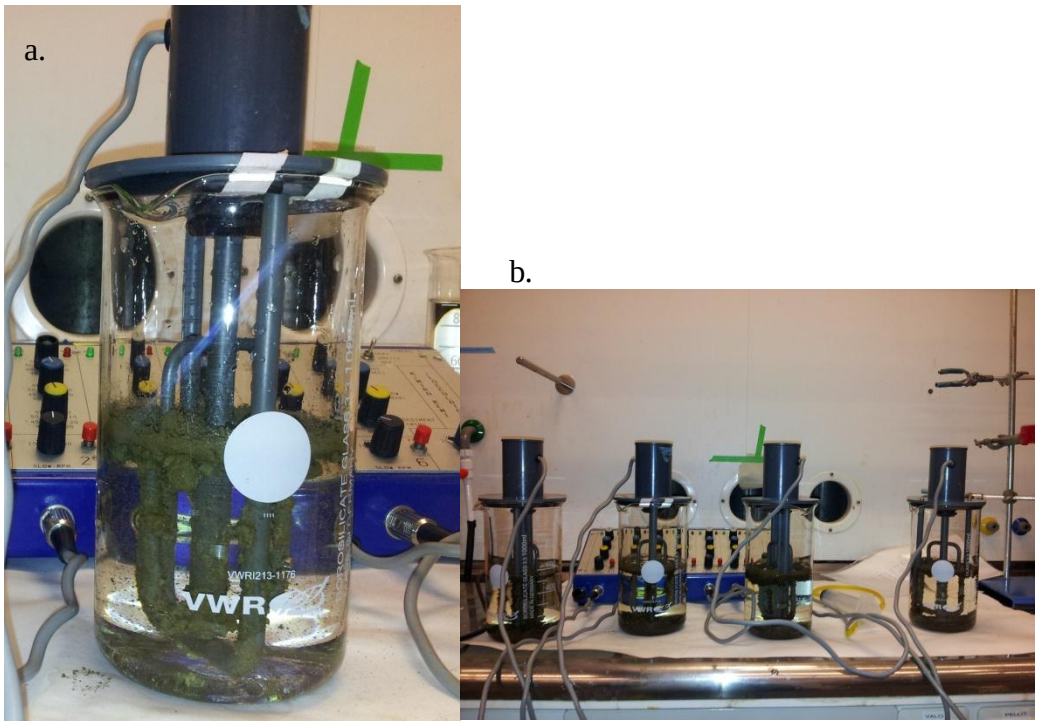


Figure 5.7 Settling experiment with vertical stirrer. a) Close-up of the vessel, to show the tendency of oil-clay to float and stick to the plastic stirrer. b) Experiment in vertical stirrer run overnight. The stirring speed was 40, 30, 20, 10 rpm from left to right.

6 DISCUSSION

The most important aspect to consider whether the studied oil-clay is suitable to be used as substrate for biogas production is the methane production potential. Also settling properties and the behavior of oil-clay in the anaerobic digestion reactor is important to consider. Nutrient levels of substrate will affect the properties of the final digestate from the reactor and its usability as fertilizer or land improver material. These issues were addressed in this study.

6.1 Methane production potential

In the assays performed methane production from oil-clay substrate varied between 532 to 664 l CH_4/kg substrate VS added and 728 to 922 l CH_4/kg substrate VS removed. The theoretical methane production potential of fats is 1000 l/kg VS (Tähti & Rintala, 2010, Wellinger et al. 2013). Compared to the theoretical methane potential, production in these settings is very efficient being close to theoretical values. Ward (2012) conducted methane production assay as co-digestion of bleaching earth by-products of the Omega 3 oil refining industry with cattle manure. Methane yields varied from 278 l/kg VS to 327 l/kg VS when 2.5 % to 12.5 % BE with cattle manure was used. The lowest yield was obtained when 12.5 % BE was added. Methane yield of cattle manure alone was not tested, but it was assumed that adding 2.5 % of BE did not have effect on the methane production. The finding was that the highest methane production was achieved when 7.5 % BE was used and higher concentrations (12.5 %) of BE started to inhibit methane production. The present study can't be directly compared to Ward's study because of different settings, but it seems that the methane production potential of BE in Ward study was significantly lower than in the present study. Cirne et al. (2007) used a model waste containing high amounts of lipids to study the effect of high lipid concentration to anaerobic digestion process. The methane production potential of model waste (lipid concentration from 5% to 47%) varied from 600 to 750 l CH_4/kg substrate VS added being at the same level as in this study.

No inhibition caused by high lipid content of methane production was seen. Some differences were seen in different inoculums used with the lag period in the initiation of methane production. The initial lag phase for methane production with thermophilic conditions was 10 days, which is considerably longer than with both mesophilic inoculums. It is possible that the microorganisms of both mesophilic inoculums were already adapted for using high lipid content as substrate. According to Angelidaki & Ahring

(1992) and Broughton et al. (1998) different inoculums are more sensitive to LCFA inhibition than others especially in the case of thermophilic inoculums. Cirne et al (2008) showed that even after a long lag phase the process can recover and methane production starts. It is also possible that the presence of clay will control the toxicity of LCFA as suggested by Angelidaki et al. (1990).

TS and VS content of oil-clay substrate were 98 and 43 % (ww) respectively. Ward (2012) used SBE from Omega 3 oil refining industry. The oil-clay used in his study had TS content of 84% and VS content of 36%. Compared to this, the oil-clay used in this present study was more rich in solid composition as well as it had higher VS content. TS removal varied from only 20 % to 48 % and VS removal was between 65 to 78 % (ww). The lowest TS removal was observed in the samples pretreated with alkali. This is due to the fact that addition of alkali prior to methane potential assay has not been calculated in the results, decreasing the TS removal from what it actually is.

Even though it was possible to show that pretreatment with alkali increased the SCOD values from 42 mg/g to over 300 mg/g sample, it did not have effect on the methane production during the assay. The benefit from alkaline treatment is probably lost once the high pH is returned to neutral in order to enable the anaerobic digestion to take place. Adjusting the pH from acidic to neutral with alkali is beneficial before feeding the oil-clay to the digester.

Thermal treatment with 37, 55 or 70ºC had no effect to the SCOD values at all. There are many examples of thermal treatment having a positive effect on sCOD release and biogas production, but the treatment efficiency is dependent on the substrate treated and the conditions of treatment (Apples et al. 2008). For example Wang et al. (2006) showed that thermal treatment of food waste was more efficient at 150 ºC than at 70 ºC. Probably more soluble COD would have been released from oil-clay samples with more stringent thermal treatment combined with pressure, but the effect to the methane potential would not increase since it was with native samples close to theoretical maximum.

6.2 Expected behavior in anaerobic digestion reactor

At least two factors are important when deciding and designing proper anaerobic digestion treatment process and conditions for producing methane from oil-clay containing mixture. pH and settleability of oil-clay are factors to take into consideration and investigate further. It is important to determine the correct portion of oil-clay from the total feed of reactor to avoid acidification and clogging of the process.

pH of oil-clay used in this study was 3.5, which is similar as Kassim et al. (2013) reported. The acidity of the SBE might be a challenge when used as feedstock for bio-

methane production. Depending on the amounts of oil-clay used in the anaerobic digestion reactor, it might be necessary to adjust the pH prior feeding it into the reactor. This could be achieved by adding alkali to the oil-clay. If it is used as a co-substrate with manure for example or if there are buffering capacity present the adjustment of pH might be avoided.

Settling properties of oil-clay substrate needs to be addressed. On the other hand oil-clay has tendency to float on the surface of water, but once it has a good mixture and good contact with water it will sink to the bottom of the vessel very fast. It is possible to control the floating and settling by using vertical stirrer as done in laboratory scale in this study, but this issue will need more intensive and thorough studies with actual reactors to be used in the methane production. Oil-clay has also the tendency to stick to the plastic parts of the stirrer and this issue needs to be addressed as well.

6.3 Nutrient levels

Nutrient, specifically, N and P, levels are low in the oil-clay substrate. N content is 0.2 % TS and P content is 0.06 % TS (TS content 98%) (personal communication with B. Toukoniitty). This would mean that if the annual production amount of oil-clay is for example 6000 tons, the oil-clay will contain 12 tons of N and 3.6 tons of P totally. The solid cattle manure contains 2.4 % N TS and 0.8 % P TS and municipal sewage sludge contains 4.0 % N TS and 2.5 % P TS (Kahiluoto et al. 2011). Even if the amount of N and P from TS in oil-clay is much lower than in solid cattle manure or in municipal sewage sludge, the high TS content makes it a valuable material to be used as fertilizer especially when nitrogen is considered. 2630 tons of solid cattle manure (19% TS) or 2500 tons of sewage sludge (12% TS) would provide the same amount of N and 2370 tons and 1200 tons respectively would provide the same amount of P as 6000 tons of oil-clay.

7 CONCLUSIONS

The aim of this study was to evaluate if oil-clay which is a by-product of oil refinery industry could be used as substrate for biogas and specifically for methane production. The amount of oil-clay produced world-wide annually is around 2 million tons and it would be beneficial if it could be used as feeding stock in anaerobic digestion instead of incineration or dumping in the landfills.

Methane potential assay showed that oil-clay is very potent substrate for anaerobic digestion. The methane production was 532 to 664 l CH_4/kg substrate VS added and 728 to 922 l CH_4/kg substrate VS removed, which is close to the theoretical value of fats. No inhibition was observed, besides differences in lag phase before methane production initiation. The methane yields when mesophilic or thermophilic inoculums were used were similar. Up to 65-78% of substrate VS added was converted to methane. Pretreatment with alkali or with different temperatures had no effect on the methane production potential.

Oil-clay settleability and pH need to be addressed when anaerobic digestion reactor and process are designed and decided. The tendency of oil-clay to float and then sink quickly to the bottom of the vessel could be controlled by proper mixing of the feeding material and inside the reactor. Acidic pH might demand adjustment prior feeding depending on the cosubstrates and portions used. It is important to determine the correct portion of oil-clay from the total feed of reactor to insure a functionality of anaerobic digestion process.

Even though the nutrient levels (N 0.2 % TS, P 0.06% TS) of oil-clay substrate are low, it still is a valuable material to be used as fertilizer after anaerobic digestion process, because of its high TS content, compared e.g. solid cattle manure or municipal sewage sludge.

As a conclusion the oil-clay mixture is a potent substrate for methane production in anaerobic digestion process. There are some challenges related to its use, but those can be overcome with more studies and careful planning. Full size reactor experiments would be needed to gather more information on the behavior of oil-clay in the anaerobic digestion.

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